

Rec'd PCT/PTO 07 MAR 2002

| | | | | | |
|--|--|---|--|---|--|
| FORM PTO-1390 (REV. 12-2001) | | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | | ATTORNEY'S DOCKET NUMBER P.19470/MAJR | |
| TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371 | | | | U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/069944 | |
| INTERNATIONAL APPLICATION NO. PCT/ZA00/00156 | | INTERNATIONAL FILING DATE 31 August 2000 (31.08.00) | | PRIORITY DATE CLAIMED 07 September 1999 (7.09.99) | |
| TITLE OF INVENTION Bioleaching of Sulphide Minerals | | | | | |
| APPLICANT(S) FOR DO/EO/US DEW, David William, et al. | | | | | |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: | | | | | |
| <p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p>a. <input type="checkbox"/> is attached hereto.</p> <p>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). Unexecuted Declaration</p> <p>10. <input checked="" type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> | | | | | |
| Items 11 to 20 below concern document(s) or information included: | | | | | |
| 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. | | | | | |
| 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. | | | | | |
| 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. | | | | | |
| 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. | | | | | |
| 15. <input checked="" type="checkbox"/> A substitute specification. | | | | | |
| 16. <input type="checkbox"/> A change of power of attorney and/or address letter. | | | | | |
| 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. | | | | | |
| 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). | | | | | |
| 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). | | | | | |
| 20. <input checked="" type="checkbox"/> Other items or information: | | | | | |
| a) PCT Published Application WO 01/18262 published 15 March 2001 | | | | | |
| b) International Search Report dated March 7, 2001 | | | | | |
| c) International Preliminary Examination Report mailed December 17, 2001 | | | | | |

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

10/069944

INTERNATIONAL APPLICATION NO.

PCT/ZA00/00156

ATTORNEY'S DOCKET NUMBER

P.19470/MAJR

21. ☒ The following fees are submitted:

CALCULATIONS PTO USE ONLY

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$1040.00

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(l)-(4) \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(l)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☒ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 130.00

| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | |
|---|--------------|--------------|------------|---------|
| Total claims | 20 - 20 = | 0 | x \$18.00 | \$ 0.00 |
| Independent claims | 2 - 3 = | 0 | x \$84.00 | \$ 0.00 |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | | + \$280.00 | \$ 0.00 |

TOTAL OF ABOVE CALCULATIONS =

\$ 1,020.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2.

\$ 0.00

SUBTOTAL =

\$ 1,020.00

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ 0.00

TOTAL NATIONAL FEE =

\$ 1,020.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$ 0.00

TOTAL FEES ENCLOSED =

\$ 1,020.00

Amount to be
refunded: \$

charged: \$

- a. ☒ A check in the amount of \$ 1,020.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 10-1213 A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Jennifer P. Yancy
Jones, Tullar & Cooper, P.C.
P.O. Box 2266
Eads Station
Arlington, VA 22202

Jennifer P. Yancy
SIGNATURE

Jennifer P. Yancy

NAME

47,003

REGISTRATION NUMBER

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | | |
|------------------------------|---|-------------------------------|
| In re Application of: |) | |
| |) | Atty. Docket No. P.19470/MAJR |
| DEW, et al. |) | |
| |) | |
| Application No.: TBA |) | |
| |) | |
| Filed: March 7, 2002 |) | |
| |) | |
| For: BIOLEACHING OF SULPHIDE |) | |
| MINERALS |) | |

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, DC 20231

Sir:

This is a Preliminary Amendment in the application filed herewith under 35 U.S.C. 371.

Please amend the above-identified application as follows:

IN THE SPECIFICATIONS:

Please cancel the specification of the subject patent application as filed. That specification corresponds to the specification of PCT/ZA00/00156, filed 31 August 2000, published as WO 01/18262 on 15 March 2001, in favor of the accompanying Substitute Specification. A marked-up copy of the specification, showing the changes made thereto to arrive at the Substitute Specification is enclosed for the Examiner's review.

IN THE CLAIMS:

Please cancel claims 1-35, all of the claims set forth in the specification of the application as filed, without prejudice.

Please add new claims 36-55, as follows:

36. A method of bioleaching a slurry containing sulphide minerals which includes the steps of subjecting the slurry in a reactor to a bioleaching process at a temperature in excess of 40°C, supplying a feed gas containing in excess of 21% oxygen by volume to the slurry, and controlling a dissolved oxygen concentration in the slurry at a level in a range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$ by controlling at least one of the following: the oxygen content of the feed gas; the supply of feed gas to the slurry; the rate of feed of slurry to the reactor.

37. The method according to claim 36 further including supplying said feed gas containing in excess of 85% oxygen by volume.

38. The method according to claim 36 further including determining said dissolved oxygen concentration in said slurry by using at least one of the following: directly measuring dissolved oxygen concentration in said slurry, measuring oxygen content in a gas above said slurry, and indirectly measuring oxygen content in off-gas from said slurry.

39. The method according to claim 36 further including the step of controlling a carbon content of said slurry.

40. The method according to claim 39 further including controlling said carbon content by at least one of the following: adding carbon dioxide gas to said slurry, and adding other carbonaceous material to said slurry.

41. The method according to claim 36 which further includes controlling a carbon dioxide content of said feed gas in a range of from 0.5% to 5.0% by volume.

42. The method according to claim 36 which further includes subjecting said slurry in said reactor to a bioleaching process at a temperature in a range of from 40°C to 100°C.

43. The method according to claim 42 wherein said temperature is in a range of from 60°C to 85°C.

44. The method according to claim 36 which further includes bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms.

45. The method according to claim 44 wherein said microorganisms are selected from the group comprising *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

46. The method according to claim 45 wherein the said microorganisms are selected from the group comprising *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

47. The method according to claim 36 further including bioleaching said slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.

48. The method according to claim 47 wherein said microorganisms are selected from the group comprising *Acidithiobacillus*; *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma*; and *Alicyclobacillus*.

49. The method according to claim 48 wherein the said microorganisms are selected from the group comprising *Acidithiobacillus caldus*; *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

50. The method according to claim 43 further including bioleaching said slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

51. The method according to claim 50 wherein said microorganisms are selected from the group comprising *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma*; *Thermoplasma*; and *Picrophilus*.

52. The method according to claim 51 wherein the said microorganisms are selected from group comprising *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

53. The method according to claim 1 wherein said reactor is substantially closed.

54. A bioleaching plant which includes a reactor vessel, a source which feeds a sulphide mineral slurry to the vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in the form of oxygen enriched air or substantially pure oxygen to the slurry, a device which measures the dissolved oxygen concentration in the slurry in the vessel, and a control mechanism whereby, in response to the said measured dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

55. The plant according to claim 54 wherein said reactor vessel is operated at a temperature in excess of 60°C.

IN THE ABSTRACT:

Please add the Abstract of the Disclosure as set forth on the separate accompanying sheet.

REMARKS

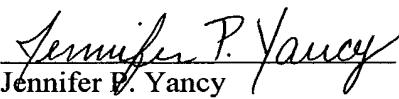
The specification of the subject patent application as filed has been canceled in favor of the accompanying Substitute Specification. The specification corresponds to the specification of PCT/ZA00/00156 filed 31 August 2000. The Substitute Specification generally places the specification in a form more in accordance with the U.S. practice. No new matter is added. A marked-up copy of the specification, which shows the changes made thereto to arrive at the Substitute Specification, is provided for the Examiner's review.

Original claims 1-35 have been canceled in favor of new claims 36-55. These newly presented claims are similar to the claims added to the PCT application and have been written in a form more in accordance with U.S. practice and eliminating multiply dependent claims.

A suitable Abstract of the Disclosure has been added. This is generally similar to the Abstract set forth in the published application WO 01/18262. No new matter is being added.

Entry of this Preliminary Amendment prior to the examination of the application on its merits, and prior to the calculation of the filing fee is respectfully requested.

Respectfully submitted,


Jennifer P. Yancy
Reg. No. 47,003

JONES, TULLAR & COOPER, P.C.
P.O. Box 2266 Eads Station
Arlington, VA 22202
(703) 415-1500
March 7, 2002

Attorney Docket No. P.19470/MAJR

ABSTRACT OF DISCLOSURE

A method of bioleaching a slurry containing sulphide minerals which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume, to the slurry, increases the rate of oxygen transfer from the gas to the liquid phase. Combined with the use of high temperatures between 50°C and 100°C and thermophile microorganisms the rate of sulphide mineral leaching is greatly enhanced.

107069944

Rec'd PCT/PTO 19 SEP 2002 #4

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | | |
|------------------------------|---|-------------------------------|
| In re Application of: |) | |
| |) | |
| DEW, et al. |) | Atty. Docket No. P.19470/MAJR |
| |) | |
| Application No.: TBA |) | |
| |) | |
| Filed: March 7, 2002 |) | |
| |) | |
| For: BIOLEACHING OF SULPHIDE |) | |
| MINERALS |) | |

SECOND PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, DC 20231

Sir:

This is a Preliminary Amendment in the application filed herewith under 35 U.S.C. 371.

Please amend the above-identified application as follows:

IN THE SPECIFICATIONS:

Please cancel the specification of the subject patent application as filed. That specification corresponds to the specification of PCT/ZA00/00156, filed 31 August 2000, published as WO 01/18262 on 15 March 2001, in favor of the accompanying Substitute Specification. A marked-up copy of the specification, showing the changes made thereto to arrive at the Substitute Specification is enclosed for the Examiner's review.

[illegible]

39. The method according to claim 36 further including the step of controlling a carbon content of said slurry.

40. The method according to claim 39 further including controlling said carbon content by at least one of the following: adding carbon dioxide gas to said slurry, and adding other carbonaceous material to said slurry.

41. The method according to claim 36 which further includes controlling a carbon dioxide content of said feed gas in a range of from 0.5% to 5.0% by volume.

42. The method according to claim 36 which further includes subjecting said slurry in said reactor to a bioleaching process at a temperature in a range of from 40°C to 100°C.

43. The method according to claim 42 wherein said temperature is in a range of from 60°C to 85°C.

44. The method according to claim 36 which further includes bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms.

45. The method according to claim 44 wherein said microorganisms are selected from the group comprising *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

46. The method according to claim 45 wherein the said microorganisms are selected from the group comprising *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

47. The method according to claim 36 further including bioleaching said slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.

48. The method according to claim 47 wherein said microorganisms are selected from the group comprising *Acidithiobacillus*; *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma*; and *Alicyclobacillus*.

49. The method according to claim 48 wherein the said microorganisms are selected from the group comprising *Acidithiobacillus caldus*; *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

50. The method according to claim 43 further including bioleaching said slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

51. The method according to claim 50 wherein said microorganisms are selected from the group comprising *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma*; *Thermoplasma*; and *Picrophilus*.

52. The method according to claim 51 wherein the said microorganisms are selected from group comprising *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

53. The method according to claim 36 wherein said reactor is substantially closed.

54. A bioleaching plant which includes a reactor vessel, a source which feeds a sulphide mineral slurry to the vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in the form of oxygen enriched air or substantially pure oxygen to the slurry, a device which measures the dissolved oxygen concentration in the slurry in the vessel, and a control mechanism whereby, in response to the said measured dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

55. The plant according to claim 54 wherein said reactor vessel is operated at a temperature in excess of 60°C.

IN THE ABSTRACT:

Please add the Abstract of the Disclosure as set forth on the separate accompanying sheet.

REMARKS

The specification of the subject patent application as filed has been canceled in favor of the accompanying Substitute Specification. The specification corresponds to the specification of PCT/ZA00/00156 filed 31 August 2000. The Substitute Specification generally places the specification in a form more in accordance with the U.S. practice. No new matter is added. A marked-up copy of the specification, which shows the changes made thereto to arrive at the Substitute Specification, is provided for the Examiner's review.

In accordance with my telephone conversation with Tamala D. Holland on September 19, 2002, claims 1-20 printed in the International Preliminary Examination Report dated 12/17/2001 have been canceled. Additional, the original claims 1-35 in WO 01/18262 have been canceled in favor of new claims 36-55. These newly presented claims are similar to the claims added to the PCT application and have been written in a form more in accordance with U.S. practice and eliminating multiply dependent claims.

A suitable Abstract of the Disclosure has been added. This is generally similar to the Abstract set forth in the published application WO 01/18262. No new matter is being added.

[illegible]

Jennifer P. Yancy
Jennifer P. Yancy
Reg. No. 47,003

Attorney Docket No. P.19470/MAJR

BIOLEACHING OF SULPHIDE MINERALSBACKGROUND OF THE INVENTION

This invention relates to the bioleaching of sulphide minerals.

5

Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen.

10 Operation at this relatively low temperature and the use of air to supply oxygen, limit the rate of sulphide mineral oxidation that can be achieved. For example carrolite and enargite are relatively slow leaching at temperatures below 50°C, and treatment at or below this temperature results in poor and sub-economic metal extraction.

15 The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is
20 such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase ^(1,2).

SUMMARY OF THE INVENTION

25 According to one aspect of the invention there is provided a method of bioleaching a slurry containing sulphide minerals which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume, to the slurry

The slurry may be an aqueous slurry containing significant quantities of sulphide minerals.

As used herein the expression "oxygen enriched gas" is intended to include a gas, eg. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume.

- 5 Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume ie. is substantially pure oxygen.

The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

15

Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

25

The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

- 5 The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.
- 10 The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase
- 15 in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

- 20 In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

- 25 In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*);
Acidithiobacillus ferrooxidans (*Thiobacillus ferrooxidans*), *Acidithiobacillus acidophilus* (*Thiobacillus*

According to a different aspect of the invention there is provided a method of bioleaching a slurry containing sulphide minerals which includes the steps of bioleaching the slurry using a suitable microorganism at a

WO 01/18262

PCT/ZA00/00156

5

temperature in excess of 40°C and controlling the dissolved oxygen concentration in the slurry within a predetermined range.

The said dissolved oxygen concentration may be controlled by controlling the supply of oxygen to the slurry.

5

The oxygen may be supplied to the slurry in the form of oxygen enriched gas or substantially pure oxygen.

The said operating temperature is preferably in the range of 60°C to 85°C.

10 The invention also extends to a method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a sulphide mineral slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume to the slurry.

The feed gas preferably contains in excess of 85% oxygen by volume.

15

The invention further extends to a method of bioleaching an aqueous slurry containing sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 40°C and maintaining the dissolved oxygen concentration in the slurry in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$

20 The dissolved oxygen concentration may be maintained by supplying gas containing in excess of 21% oxygen by volume to the slurry. The temperature is preferably in the range of from 60°C to 85°C.

The invention is also intended to cover a bioleaching plant which includes a reactor vessel, a source which feeds a sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved
25 oxygen concentration in the slurry in the vessel, and a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range.

Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen content or concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

5

As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred to make use of suitable measurement probes to sample the actual values of the critical parameters.

10

For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

15

A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, eg. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry.

20

Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

25

The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by way of example with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a portion of a plant in which the invention is carried out, and

5 Figures 2, 3 and 4 reflect various results and parameters obtained from operating a bioreactor using the principles of the invention.

DESCRIPTION OF PREFERRED EMBODIMENT

10 General Principles

The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits the rate of reaction, requires enrichment of the air with oxygen ie. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use
15 of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of the oxygen to warrant the additional expense ⁽³⁾; and
- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral
20 bioleaching stops ⁽⁴⁾.

Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

25

The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon

dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

$$R = M \cdot (C^* - C_L) \quad (1)$$

where: R = Oxygen demand as mass (kg) per unit volume (m^3) per unit time(s) ($kg/m^3/s$),

M = Oxygen mass transfer coefficient in reciprocal seconds (s^{-1}),

C^* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m^3) (kg/m^3),
and

C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3) (kg/m^3).

The factor $(C^* - C_L)$ is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer coefficient (M) or the oxygen driving force $(C^* - C_L)$ must be increased.

An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach, however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen content or concentration C_L .

Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

WO 01/18262

PCT/ZA00/00156

9

The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$

On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$

As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C . *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C .

The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C :

increases the specific sulphide oxidation duty of the reactor considerably;

results in an unexpected and significantly enhanced oxygen mass transfer rate;

increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the point where microorganism growth and mineral oxidation are prevented and below the point at which microorganism growth is inhibited; and

the overall power required for the oxidation of sulphide minerals is significantly reduced.

The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

- 5 The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m³ in volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation
- 10 is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low dissolved oxygen concentrations in the solution phase.

- It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the
- 15 use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

- 20 Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

- In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may
- 25 be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.

Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

5 Table 1 Commercial Bioreactor Performance Results

| Description | Units | Plant A | Plant B |
|---|------------------------|---------|---------|
| Reactor temperature | °C | 42 | 40 |
| Reactor operating volume | m ³ | 471 | 896 |
| Oxygen utilisation | % | 37.9 | 43.6 |
| Typical dissolved oxygen concentration | mg/l | 2.5 | 2.7 |
| Oxygen mass transfer coefficient | s ⁻¹ | 0.047 | 0.031 |
| Specific oxygen demand | kg/m ³ /day | 21.6 | 14.8 |
| Specific sulphide oxidation duty | kg/m ³ /day | 8.9 | 5.7 |
| Specific power consumption per kg sulphide oxidised | kWh/kgS ²⁻ | 1.7 | 1.8 |

At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors. Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

Table 2 Predicted Improvement In Commercial Bioreactor Performance

| | Units | Plant A – typical operation | Plant A - using the method of the invention |
|---|------------------------|-----------------------------|---|
| Reactor temperature | °C | 42 | 77 |
| Microbial type strain | - | <i>Acidithiobacillus</i> | <i>Sulfolobus</i> |
| Inlet gas oxygen content | % by volume | 20.9 | 90.0 |
| Oxygen utilisation | % | 37.9 | 93.0 |
| Typical dissolved oxygen concentration | mg/l | 2.5 | 2.5 |
| Specific oxygen demand | kg/m ³ /day | 21.6 | 59.5 |
| Specific sulphide oxidation duty | kg/m ³ /day | 8.9 | 24.5 |
| Specific power consumption per kg sulphide oxidised | kWh/kgS ²⁻ | 1.7 | 1.2 |

The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

Particular Example

Figure 1 of the accompanying drawings illustrates a non-limiting example of the invention and shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady supply of oxygen and a

variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry 20.

5

Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

15

Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry ie. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

20

Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

25

Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry

It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways eg. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas ie. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen ie. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in

Figure 2. If the dissolved oxygen concentration is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of greater than 2 g/l. At consistent levels of biooxidation, achieved by maintaining a dissolved oxygen concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a temperature of 77°C, with *Sulfolobus*-like archaea.

The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range 0.4×10^{-3} kg/m³ to 3.0×10^{-3} kg/m³. The results of the experiment are presented in Figure 3.

From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of 0.4×10^{-3} kg/m³ to 3.0×10^{-3} kg/m³, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum

of 90.8% the specific oxygen demand was increased from 11.3 kg/m³/day to 33.7 kg/m³/day. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained microorganism growth, the oxygen utilisation was maximised. The oxygen utilisation showed a general increase with an increase in the oxygen content of the inlet gas from 29% (for an inlet gas oxygen content of 20.7%) to 91% (for inlet gas containing 85.5% oxygen)

The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C, according to the temperature correction factor proposed by Smith et al ⁽⁵⁾. This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C ⁽⁶⁾.

The determination of the enhanced oxygen mass transfer coefficient is shown from the results presented in Figure 4, where the oxygen demand divided by the design oxygen mass transfer coefficient (M_{design}) is plotted against the oxygen driving force, as defined in equation (1). The slope of the regression line plotted through the data indicates the enhancement in the oxygen mass transfer coefficient by a factor of 2.69.

INT 1006/MAJR/2™

1

CLAIMS

1. A method of bioleaching a slurry containing sulphide minerals which includes the steps of subjecting the slurry in a reactor to a bioleaching process at a temperature in excess of 40°C, supplying a feed gas containing in excess of 21% oxygen by volume to the slurry, and controlling the dissolved oxygen concentration in the slurry at a level in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$ by controlling at least one of the following: the oxygen content of the feed gas; the supply of feed gas to the slurry; the rate of feed of slurry to the reactor.
2. A method according to claim 1 wherein the feed gas contains in excess of 85% oxygen by volume.
3. A method according to claim 1 or 2 wherein the dissolved oxygen concentration in the slurry is determined by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen in a gas above the slurry, and indirectly, by measurement of the oxygen content in off-gas from the slurry.
4. A method according to any one of claims 1 to 3 which includes the step of controlling the carbon content of the slurry.
5. A method according to claim 4 wherein the said carbon content is controlled by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.
6. A method according to any one of claims 1 to 5 which includes the step of controlling the carbon dioxide content of the feed gas in the range of from 0.5% to 5.0% by volume.
7. A method according to any one of claims 1 to 6 wherein the bioleaching process is carried out at a temperature in the range of from 40°C to 100°C.

INT 1005/MAJR/2nd

2

8. A method according to claim 7 wherein the said temperature is in the range of from 60°C to 85°C.
9. A method according to any one of claims 1 to 6 which includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms.
- 5 10. A method according to claim 9 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.
- 10 11. A method according to claim 9 or 10 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.
- 15 12. A method according to any one of claims 1 to 7 which includes the step of bioleaching the slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.
- 20 13. A method according to claim 12 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus* (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.
- 25 14. A method according to claim 12 or 13 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.
15. A method according to claim 8 which includes the step of bioleaching the slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

INT 1006/MAJR/2nd

3

16. A method according to claim 15 wherein the microorganisms are selected from the following genus groups: *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.
- 5 17. A method according to claim 15 or 16 wherein the said microorganisms are selected from the following species: *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.
- 10 18. A method according to any one of claims 1 to 17 wherein the reactor is substantially closed.
- 15 19. A bioleaching plant which includes a reactor vessel, a source which feeds a sulphide mineral slurry to the vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in the form of oxygen enriched air or substantially pure oxygen to the slurry, a device which measures the dissolved oxygen concentration in the slurry in the vessel, and a control mechanism whereby, in response to the said measured dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.
- 20 20. A plant according to claim 19 wherein the reactor vessel is operated at a temperature in excess of 60°C.

REFERENCES

1. Bailey, A.D., and Hansford, G.S., (1996), Oxygen mass transfer limitation of batch bio-oxidation at high solids concentration. *Minerals Eng.*, 7(23), pp293-303.
2. Myerson, A.S., (1981), Oxygen mass transfer requirements during the growth of *Thiobacillus ferrooxidans* on iron pyrite, *Biotechnol, Bioeng.*, Vol 23, pp1413.
3. Peter Greenhalgh, and Ian Ritchie, (1999); Advancing Reactor Design For The Gold Bioleach Process; Minproc Ltd, Biomine 99, 23-25 Aug 1999, Perth Australia, pp52-60.
4. Brock Biology of Microorganisms, Eight Edition, 1997., Madigan M.T., Martinko J.M., Parker J., Prentia Hall International, Inc., London.
5. J.M. Smith, K van't Riet and J.C. Middleton, (1997), Scale-Up of Agitated Gas-Liquid Reactors for Mass Transfer, in Proceedings of the 2nd European Conference on Mixing, Cambridge, England, 30 March – 1 April 1997, pp.F4-51 – F4-66.
6. Boogerd, F. C., Bos, P., Kuenen, J. G., Heijnen, J. J. & Van der Lans, R. G. J. M, Oxygen and Carbon Dioxide Mass Transfer and the Aerobic, Autotrophic Cultivation of Moderate and Extreme Thermophiles : A Case Study Related to the Microbial Desulfurization of Coal, *Biotech. Bioeng* , 35, 1990, p. 1111 – 1119.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 March 2001 (15.03.2001)

PCT

(10) International Publication Number
WO 01/18262 A3

(51) International Patent Classification⁷: C22B 3/18, 3/02

(21) International Application Number: PCT/ZA00/00156

(22) International Filing Date: 31 August 2000 (31.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99/5746 7 September 1999 (07.09.1999) ZA

(71) Applicant (for all designated States except US): **BILLITON INTELLECTUAL PROPERTY B.V.** [NL/NL];
Mariahoeveplein 6, NL-2509 AA The Hague (NL).

(74) Agent: **MCCALLUM RADEMEYER & FREIMOND**;
P.O. Box 1130, 7 June Avenue, Bordeaux, 2125 Randburg
(ZA).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **DEW, David, William** [ZA/ZA]; 200 Hans Strijdom Drive, 2194 Randburg (ZA). **BASSON, Petrus** [ZA/ZA]; 200 Hans Strijdom Drive, 2194 Randburg (ZA).

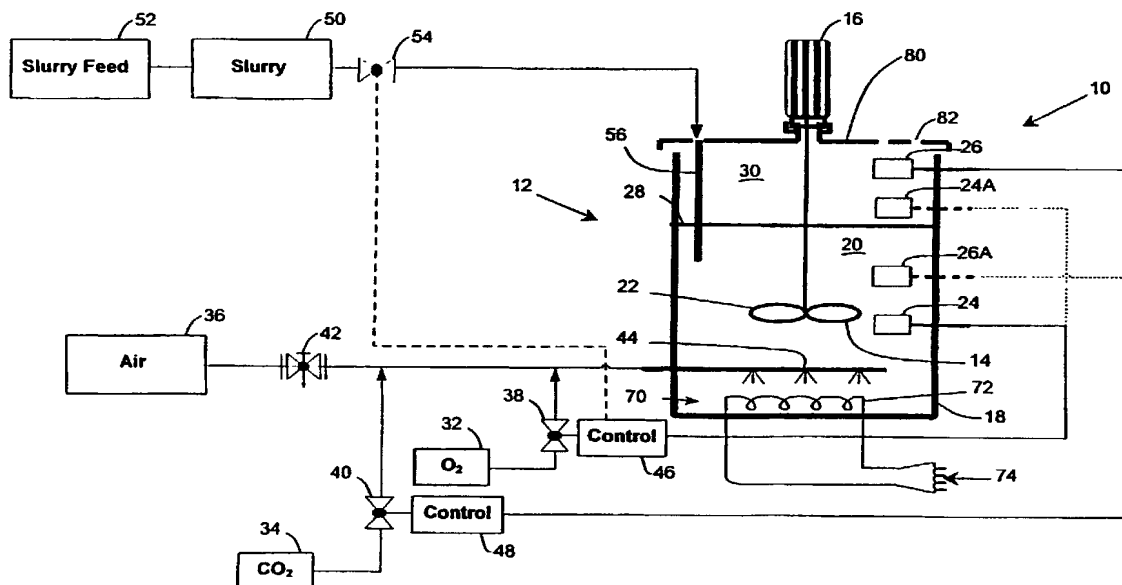
Published:

— With international search report.

(88) Date of publication of the international search report:
31 May 2001

[Continued on next page]

(54) Title: BIOLEACHING OF SULPHIDE MINERALS



(57) Abstract: A method of bioleaching a slurry containing sulphide minerals which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume, to the slurry, increases the rate of oxygen transfer from the gas to the liquid phase. Combined with the use of high temperatures between 50 °C and 100 °C and thermophile microorganisms the rate of sulphide mineral leaching is greatly enhanced.

WO 01/18262 A3

10/069944

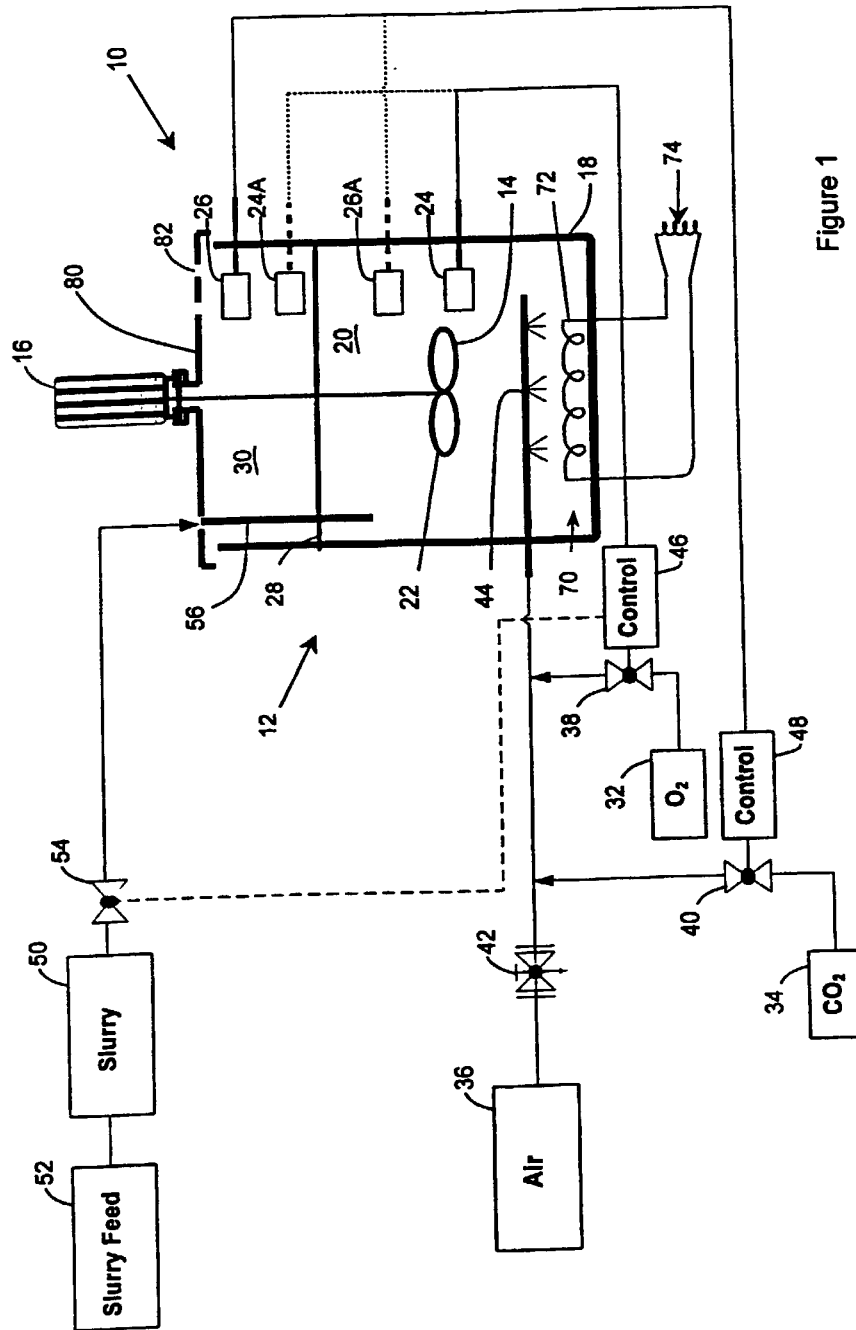


Figure 1

10/069944

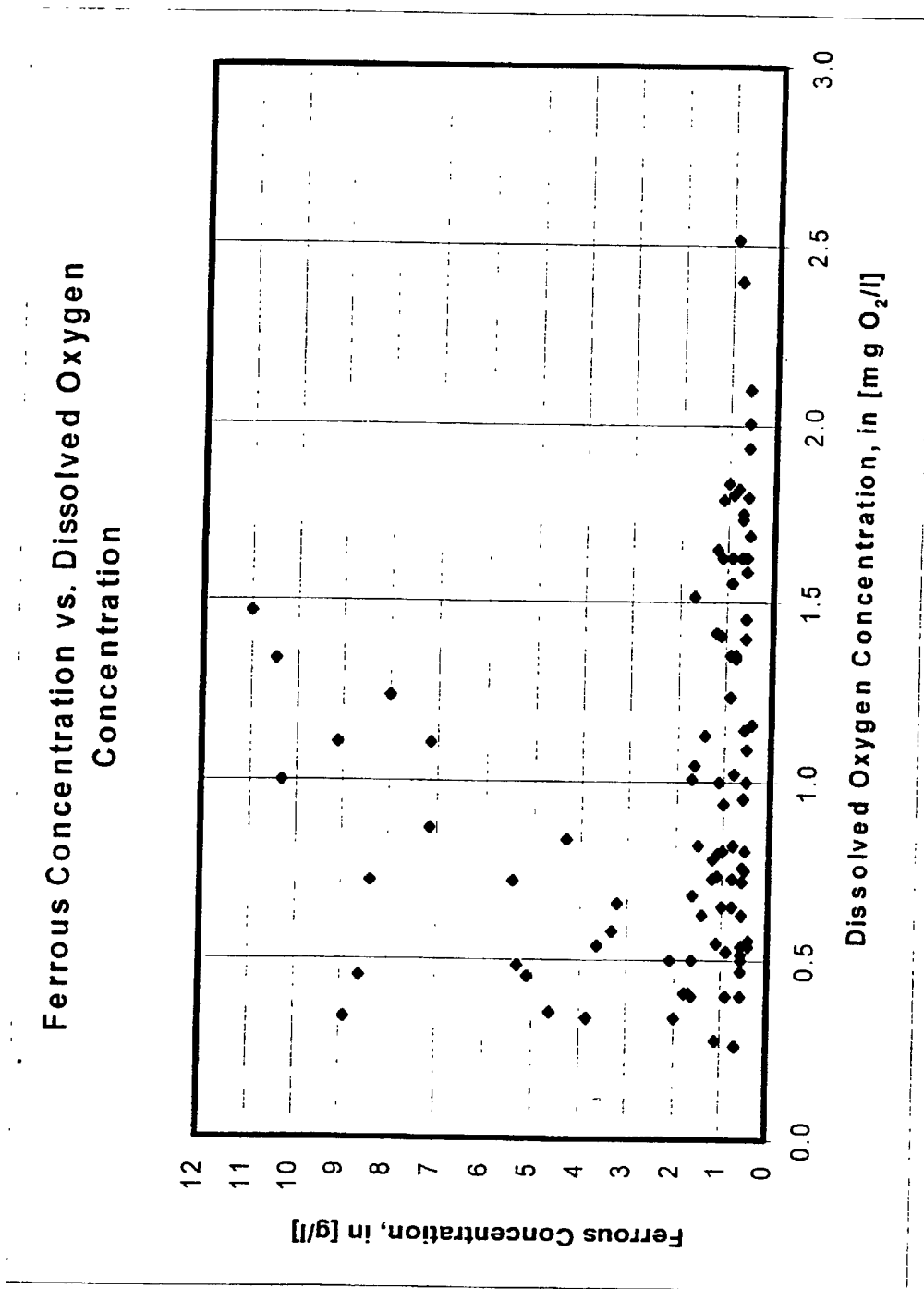


Figure 2 Results Showing The Effect of Reduced Microbial Oxidation On Iron(II) Concentration Levels In Solution As A Result Of Operating At Low Dissolved Oxygen Concentrations

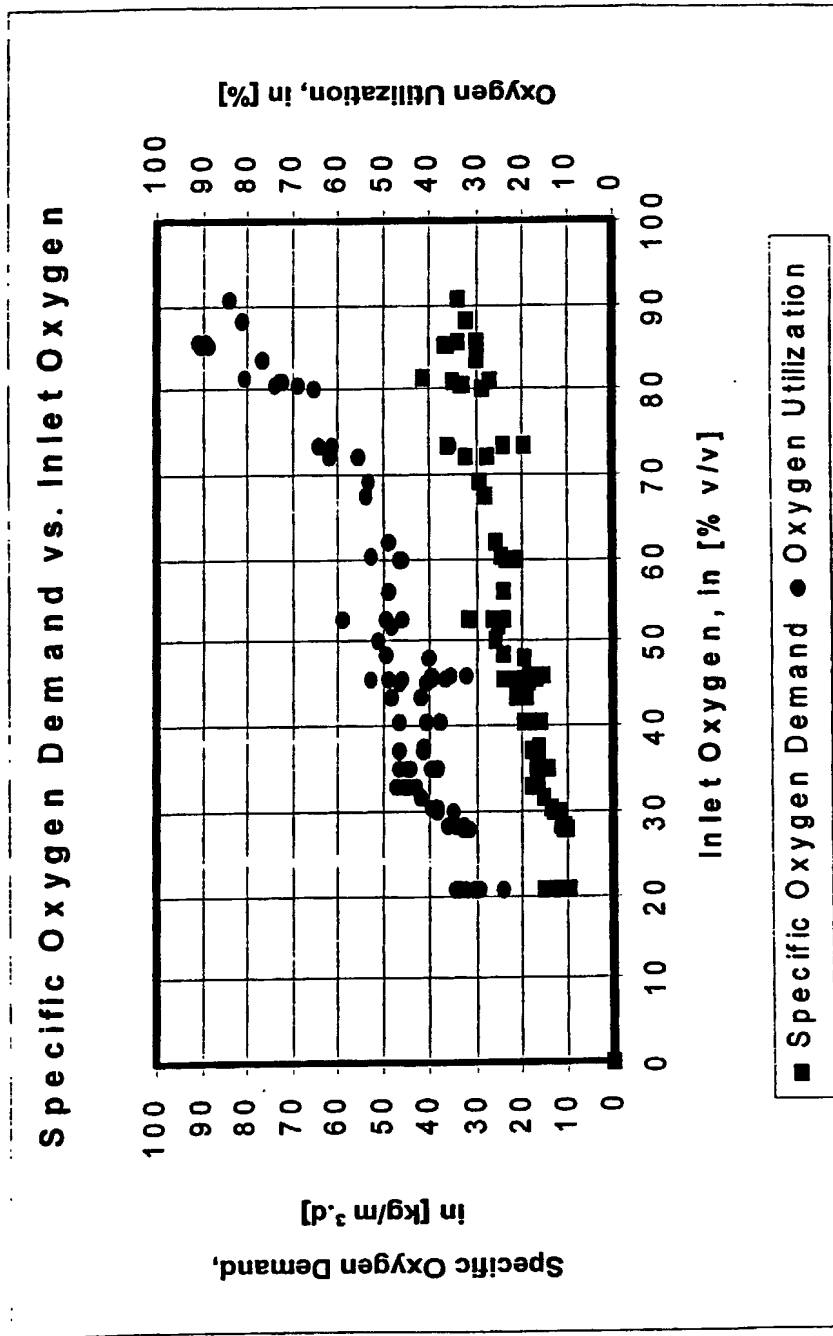


Figure 3 Results Showing The Increase In Specific Oxygen Demand and Oxygen Utilisation Achieved By Increasing The Oxygen Content Of The Inlet Gas Under Controlled Conditions By The Method Of The Invention

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

This declaration is of the following type:

- ☐ original
- ☐ design
- ☐ supplemental
- ☒ national stage of PCT
- ☐ divisional
- ☐ continuation
- ☐ continuation-in-part (CIP)

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed for and for which a patent is sought on the invention entitled:

Bioleaching of Sulphide Minerals

the specification of which

- ☐ is attached hereto
- ☐ was filed on _____, as
Application No. _____
and was amended on _____
(if applicable)
- ☒ was described and claimed in PCT International Application No. ZA00/00156
filed on 31 August 2000 and as amended under PCT Article 19 on _____ (if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any Amendment referred to above.

I acknowledge duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

- ☐ In compliance with this duty there is attached an Information Disclosure Statement. 37 CFR 1.97.

[illegible]

☐ no such applications have been filed
☒ such applications have been filed as follows.

Prior Foreign Application(s)

| | | | |
|-----------------------|-----------------------|--------------------------|--|
| <u>99/5746</u> | <u>South Africa</u> | <u>07 September 1999</u> | <input checked="" type="checkbox"/> <input type="checkbox"/> |
| (Number) | (Country) | (day/month/year filed) | Yes No |
| <u> </u> | <u> </u> | <u> </u> | <input type="checkbox"/> <input type="checkbox"/> |
| (Number) | (Country) | (day/month/year filed) | Yes No |

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

| | |
|----------------------|---------------|
| (Application Number) | (Filing Date) |
| (Application Number) | (Filing Date) |

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below, and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose all information known to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

| (Application No.) | (Filing Date) | (patented, pending, abandoned) |
|-------------------|---------------|--------------------------------|
| (Application No.) | (Filing Date) | (patented, pending, abandoned) |

14 10
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agents to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

George M. Cooper, Reg. No. 20,201
Felix J. D'Ambrosio, Reg. No. 25,721
William A. Blake, Reg. No. 30,548

Eric S. Spector, Reg. No. 22,495
Douglas R. Hanscom, Reg. No. 26,600
Jennifer P. Yancy, Reg. No. 47,003 (6)

Send correspondence to

Jennifer P. Yancy
JONES, TULLAR & COOPER, P.C.
P.O. Box 2266 Eads Station
Arlington, VA 22202

Direct telephone calls to

Jennifer P. Yancy
(703) 415-1500

I hereby declare all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00 Full name of sole or first inventor DEW, David William

Inventor's signature X [Signature] 15 March 2002

Residence Randburg, Republic of South Africa ZAX (Date)

Citizenship X SOUTH AFRICAN

Post Office Address 200 Hans Strijdom Drive, Randburg, 2194, Republic of South Africa

2-00 Full name of second joint inventor, if any BASSON, Petrus

Inventor's signature X [Signature] 19 March 2002

Residence Randburg, Republic of South Africa ZAX (Date)

Citizenship X South African

Post Office Address 200 Hans Strijdom Drive, Randburg, 2194, Republic of South Africa